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FINAL TECHNICAL REPORT

Chemical and Biological Variability in the Upper Water Column

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INTRODUCTION

This program, which has evolved over more than ten years, has had a long-term goal to document and understand chemical and biological variability in the upper water column of the world's oceans. In the final years of the project a major thrust was to develop methods that would more adequately link chemical and biological distributions in the marine environment. To this end an emphasis was placed on developing techniques and measuring photosynthetic pigment distributions as indicators of biological activity in the ocean. These investigations (1) developed and improved the methodologies for measurements of chlorophyll and carotenoid pigments, (2) improved the use of pigments as chemotaxonomic indicators, (3) investigated physical-chemical-biological interactions in frontal areas, (4) increased our understanding of the photo-adaptive strategies of marine phytoplankton, (5) documented unique and novel physiological functions for pigments, and (6) evaluated potential new and more powerful pigment analytical techniques.

OBJECTIVES

A primary objective in the later phases of this program was to improve the resolution, accuracy and precision of pigment measurements. Secondary objectives were to develop models of pigment distributions and compositions based on laboratory experiments, field programs, and cultures. Pigment distributions were also measured in support of a number of major oceanographic investigations. Finally, potential new pigment analytical techniques were evaluated.

TASKS COMPLETED

Several major collaborative investigations have been finalized and the results published (see publications). A particle beam liquid chromatograph interface for mass spectrometry (LC/MS) and supercritical fluid chromatography (SFC) were evaluated as potential analytical improvements for pigment analysis. Evaluation of instrumental operating conditions, sensitivity, detectors, and column resolution suggested that little if any improvement in analyses were provided by the present LC/MS or SFC technology. Numerous results of this program have been reported over the years and only the most recent program accomplishments are summarized

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here. The reader is referred to the many publications that have resulted from this program.

RESULTS

The following represent the latest in a series of research results:

- (1) Water masses in the North Pacific Ocean were classified based on phytoplankton pigment assemblages into oligotrophic, highly productive and transitional (*Deep-Sea Research*, 1991, 38: 243-266).
- (2) The distribution of pigments in the Bering and Chukchi Seas were determined to be complex and variable due to the non-uniform distribution of both total biomass and community composition (*U.S. Fish Wildl. Serv. Biol. Rep.* 90(13): 97-113).
- (3) A high degree of structural diversity in plant pigments allows for the development of sensitive chemotaxonomic indicators. An ever increasing number of unique pigments are being identified and their occurrence and structure has been related to biochemical function. (*Energy and Fuels*, 1990, 4: 653-657; *J. Phycol.*, in press).
- (4) Nutrient loading, transport of coastal seed populations and elevated attenuation coefficients were shown to contribute to the Orinoco River's influence on phytoplankton composition and distribution in the Caribbean Sea (*J. Geophys. Res.*, 1993, in press).

ACCOMPLISHMENTS

The development, improvement, and standardization of pigment analytical techniques during this study has led to the widespread use of plant pigments as a fundamental oceanographic measurement. Chlorophyll and carotenoid distributions are basic to understanding biogeochemical cycling, particle distributions, and optical properties in the upper water column. Accurate and precise measurement techniques have been developed by the application of knowledge from a diverse range of fields providing oceanographers with substantially enhanced, state-of-the-art analytical capabilities. The following is an updated list of publications and presentations related to this project since 1989.

1989 Publications

Bidigare, R.R. 1989: Determination of chlorophylls and their derivatives by high-performance liquid chromatography (HPLC) In: *Standard Methods for the Examination of Water and Wastewater*. 17th Edition. American Public Health Association, Section 10, 36-39.

- Bidigare, R.R. 1989: Photosynthetic pigment composition of the brown tide alga: unique chlorophyll and carotenoid derivatives. In: *Coastal and Estuarine Studies*, Vol. 35 (E. Cosper, E. Carpenter and M. Bricelj, Eds.), Springer-Verlag, Berlin, pp. 57-75.
- Smith, R.C., B. Prezelin, R.R. Bidigare and K.S. Baker. 1989: Bio-optical modeling of photosynthetic production in coastal waters. *Limnol. Oceanogr.*, 34, 1526-1546.
- Shapiro, L.P., E.M. Hauger, M.D. Keller, R.R. Bidigare, L. Campbell and R.R. Guillard. 1989. Taxonomic affinities of marine coccoid ultraplankton: A comparison of immunochemical surface antigen cross-reactions and HPLC chloroplast pigment signatures. *J. Phycol.*, 25, 794-797.
- Bidigare, R.R., O. Schofield and B.B. Prezelin. 1989. Influence of zeaxanthin on quantum yield of photosynthesis of *Synechococcus* Clone WH7803 (DC2). *Mar. Ecol. Progr. Ser.*, 56, 177-188.
- Bidigare, R.R. 1989. Potential effects of UV-B radiation on marine organisms of the Southern Ocean: distribution of phytoplankton and krill during austral spring. *Photochem. Photobiol.*, 50, 469-477.
- Biggs, D.C., S.P. Berkowitz, M.A. Altabet, R.R. Bidigare, D.J. DeMaster, S.A. Macko, M.E. Ondrusek and I. Noh. 1989. A cooperative study of upper ocean particulate fluxes. In: *Proceedings of the Ocean Drilling Program, Part A, Initial Report, Leg 119*, pp. 109-120.
- Powell, E.N., A.C. Morrill and R.R. Bidigare. 1989. Catalase in sulfide- and methane-dependent macrofauna from petroleum seeps. *Experientiae*, 45, 198-200.
- Brooks, J.M., M.C. Kennicutt II, I.R. MacDonald, D.L. Wilkinson, N.L. Guinasso Jr. and R.R. Bidigare. 1989. Gulf of Mexico hydrocarbon seep communities. IV. Descriptions of known chemosynthetic communities. In: *Proceedings of the Offshore Technology Conference*, pp. 663-667.

1990 Publications

- MacDonald, I.R., J.F. Reilly, N.L. Guinasso, J.M. Brooks, R.S. Carney, W.A. Bryant and T.J. Bright. 1990. Chemosynthetic mussels at a brine-filled pockmark in the northern Gulf of Mexico. *Science*, 248:, 1096-1099.
- Schofield, O., R.R. Bidigare and B.B. Prezelin. 1990. Chromatic photoadaptation and enhancement effects on wavelength-dependent quantum yield and productivity in the diatom *Chaetoceros gracile* and the prymnesiophyte *Emillania huxleyi*. *Mar. Ecol. Progr. Ser.*, 64, 175-186.

- Bidigare, R.R., J. Marra, T.D. Dickey, R. Iturriaga, H. Pak and R.C. Smith. 1990. Evidence of photoplankton succession and chromatic adaptation in the Sargasso Sea during springtime 1985. *Mar. Ecol. Progr. Ser.*, 60, 113-122.
- Bidigare, R.R. 1990. Pigment composition and phytoplankton biomass. In: *Results of the Second U.S.-U.S.S.R. Bering Sea Expedition, Summer 1984* (P.F. Roscigno, ed.), U.S. Fish Wildl. Serv. Biol. Rep. 90 (13), pp. 97-113.
- Bidigare, R.R., M.C. Kennicutt II, M.E. Ondrusek, M.D. Keller, and R.R.L. Guillard. 1990. Novel chlorophyll-related compounds in marine phytoplankton: Distributions and geochemical implications. *Energy & Fuels* 4: 653-657.

1991 Publications

- Ondrusek, M.E., R.R. Bidigare, S.T. Sweet, D.A. DeFreitas, and J.M. Brooks. 1991. Distribution of algal pigments in the North Pacific Ocean in relation to physical and optical variability. *Deep-Sea Res.* 38: 243-266.
- Bidigare, R.R. M.C. Kennicutt II, W.L. Keeney-Kennicutt, and S.A. Macko. 1991. Isolation and purification of chlorophylls *a* and *b* for the determination of stable carbon and nitrogen isotope compositions. *Anal. Chem.* 63: 130-133.

1992 Publications

- Kennicutt II, M.C., R.R. Bidigare, S.A. Macko and W.L. Keeney-Kennicutt. 1992. The stable isotopic composition of photosynthetic pigments and related biochemicals. *Chem. Geol.* 101: 235-245.
- Kennicutt II, M.C., S.A. Macko, H.R. Harvey, and R.R. Bidigare. 1992. Preservation of *Sargassum* under anoxic conditions: Molecular and isotopic evidence. In: *Organic Matter: Productivity, Accumulation and Preservation in Recent and Ancient Sediments* (J.K. Whelan, J.W. Farrington, eds.), Columbia University Press, New York, pp. 123-141.
- Kennicutt, M.C., R.R. Bidigare, and S.A. Macko. 1992. The molecular stable isotopic composition of chlorophyll *a*: A conceptual approach. In: *Southern Ocean Process Study*, U.S. JGOFS Planning Report Number 1G, U.S. JGOFS Planning and Coordination Office, Woods Hole, MA, pp. 85-94.
- Bidigare, R.R., M.E. Ondrusek, and J.M. Brooks. 1992. Distributions of algal pigments in near-surface waters of the Bering and Chukchi Seas. In: *Results of the Third Joint U.S.-U.S.S.R. Bering & Chukchi Seas*

Expedition (BERPAC), Summer 1988 (P.A. Nagel, ed.), U.S. Fish Wildl. Serv., Washington, DC, pp. 127-135.

1993 Publications

Bidigare, R.R., M.E. Ondrusek, M.C. Kennicutt II, R. Iturriaga, H.R. Harvey, S.A. Macko and R. Hoham. 1993. Evidence for a photoprotective function for secondary carotenoids of snow algae. *J. Phycol.* (in press).

Bidigare, R.R., M.E. Ondrusek, and J.M. Brooks. 1993. Influence of the Orinoco River outflow on distributions of algal pigments in the Caribbean Sea. *J. Geophys. Res.* (in press).

1989 Presentations

Brooks, J.M., M.C. Kennicutt II and R.R. Bidigare. Studies of hydrocarbon seep communities on the Texas/Louisiana continental slope. OTC Meeting, May 1989 (Houston).

Kennicutt II, M.C., H.R. Harvey, S.A. Macko and R.R. Bidigare. Anoxic hypersalinity: A modern analogy for the preservation of organic matter over geologic time. 14th International Meeting on Organic Geochemistry, September 1989 (Paris).

Kennicutt II, M.C., S.A. Macko and R.R. Bidigare. $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ of porphyrins: Sensitive indicators of biochemical fractionation and organic matter sources. 14th International Meeting on Organic Geochemistry, September 1989 (Paris).

1990 Presentations

Ondrusek, M.E., R.R. Bidigare, and S.T. Sweet. Distributions of algal pigments in the Caribbean Sea: A two layer system. Winter AGU/ASLO Meeting, 12-16 February 1990 (New Orleans).

Bidigare, R.R. and M.C. Kennicutt II. Novel chlorophyll c compounds in "primitive" bloom producing species of golden brown algae and their geochemical implication. Porphyrin Geochemistry Symposium, National ACS Meeting, April 22-27, 1990. (Boston, Invited)

Bidigare, R.R. and M.C. Kennicutt II. A multi-functional role for carotenoid-fatty acid esters in Antarctic snow algae. Southern Regional Geochemistry Meeting, May 1990 (College Station).

Bidigare, R.R., M.C. Kennicutt II, H.R. Harvey and S.A. Macko. Distributions and possible functions of secondary carotenoid esters in snow algae. Poster Session, 1990 Gordon Conference on Organic Geochemistry, August 1990 (Holderness School)

1991 Presentations

Macko, S.A., D.C. Biggs, R.R. Bidigare, M.A. Altabet, and D.J. DeMaster.
Upper water column sediment trap particulate fluxes, chemical
characterization, and state of preservation: Results from ODP Legs
113 and 199. International Conference on the Role of the Southern
Ocean and Antarctica in Global Change: An Ocean Drilling Perspective,
28-30 August 1991 (Santa Barbara).

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